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Citation style: Kądziołka-Gaweł Mariola, Smołka-Danielowska Danuta. (2017). 57Fe Mössbauer spectroscopy investigations of iron phase composition in fluidized beds from the ELCHO power plant in Chorzów, Poland. "Nukleonika" (Vol. 62, iss. 2 (2017), s. 101-107), doi 10.1515/nuka-2017-0014

NUKLEONIKA 2017;62(2):101–107
doi: 10.1515/nuka-2017-0014

ORIGINAL PAPER

^{57}Fe Mössbauer spectroscopy investigations of iron phase composition in fluidized beds from the ELCHO power plant in Chorzów, Poland

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Abstract. The study investigates the physical and chemical properties of fly ash and bottom ash from a power plant ELCHO in Chorzów, Poland. Coal combustion products generated in the process of combustion in circulating fluidized beds (CFBs) are considerably different from fly and bottom ashes obtained from dust furnaces and multi-layer ones. The composition of the iron-bearing phase in the waste of circulating fluidized bed combustion was determined using Mössbauer spectroscopy and X-ray powder diffraction (XRD) methods.

Keywords: Mössbauer spectroscopy • fly ash • bottom ash

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Received: 22 June 2016
Accepted: 15 October 2016

Introduction

The power sector is the main consumer of hard coal (about 61%) in Poland. The technology of fluidized bed combustion is attractive as far as technological and economic aspects are concerned, but it is not an easy process, because of the need for an appropriate choice of sorbent and the graining of it. It is characterized by a relatively low temperature of the process of combustion within the range of 850–950°C, which minimizes the synthesis of oxides from the air. The specificity of fluidized-bed furnaces enables combustion not only of traditional fuels, but also of other materials, such as: residues, post-flotation waste and spoil (formed during the processes of the mining and enrichment of hard coal). Fluidized-bed boilers containing circulating fluidized beds are the most common in combined heat and power plants in Poland and European countries, because they live up to high expectations concerning environmental protection [1–3]. Bottom ash (30–60%) following graining of 0.3–5.6 mm and fly ash (40–70%) produced by dedusting devices over a wide range of graining (1–300 μm) constitute waste from the technology of fluidized-bed combustion. Frequently increased amounts of fly ash (20–80%), caused primarily by the combustion of poor-quality hard coals and high amounts of compounds, which is soluble in water, is a disadvantage of fluidized-bed combustion [4].

Solid products, which arise during the combustion of fuels, differ substantially from the fly ashes and cinders which originate from dust and multi-layer furnaces. They mainly refer to the mineral composition and morphology of grains, as well as

to the grain composition. The chemical composition of waste from different power plants can differ depending on the kind of fuel used [5, 6]. Fluidized ashes usually contain a higher content of calcium as an oxide and as a sulphate [7]. The urban air particulates contain iron, and some of the pathological effects caused after their inhalation may be due to reactive oxygen species produced by iron-catalysed reactions [8, 9]. The potential sources of iron in the atmosphere are multifarious. However, ultrafine iron can be emitted from coal burning power plants where iron is present in the mineral matter of the fuel. In this case, the ultrafine iron can be emitted into the atmosphere in the form of an ultrafine aerosol in association with residual amounts of soot. While soils exhibit relatively low levels of solubility in iron, the high solubility of atmospheric iron observed in field studies has been explained by the atmospheric chemical processing of dust particles during long-distance transportation [10]. Also, it was suggested from *in vitro* studies that ferric iron in an aluminosilicate glass phase served as the source of bio-available iron from coal fly ash and that the process of making iron bio-available depends on the size of ash particles [11, 12].

Mössbauer spectroscopy has been applied to a great variety of problems related to coal usage, as excellently reviewed in [13, 14]. In the present paper, the iron-bearing phase composition in circulating fluidized beds from the ELCHO power plant in Chorzów were determined from Mössbauer spectroscopy and X-ray powder diffraction (XRD) methods.

Samples and experiment

Samples of fly and bottom fluidized ashes originated from the combustion of hard coal in the circulating fluidized bed (CFB) of the ELCHO Combined Heat and Power Plant in Chorzow of the Upper Silesian Industrial Region in Poland. Hard coal following 0–20 mm of graining was combusted in the steam boilers – type CFB Compact OF-420/13,9/540/230, which contain an atmospheric hearth and facilitate the natural circulation of water. The calorific value of hard coals was equal to 16–19 MJ/kg and the range of ash content was 18–30%. The temperature during the process of combustion reached 890°C. The electro filters are dedusting devices with an effectiveness of dedusting amounting to 96–97%. Altogether 10 samples were taken. Each of them weighed about 2 kg. There were five samples of fly fluidized ashes (marked with the symbols 1l–5l) and bottom fluidized ashes (marked with the symbols 1d–5d) each.

The samples were examined by X-ray powder diffraction using Co-Kα_1 radiation (from a graphite monochromator) in a Philips PW 3710 diffractometer to determine the abundance of the most common crystalline components of the fluidized ashes. The duration of impulse counting in the step method was 3 seconds (per step), counter speed was 0.01–0.02° per minute, lamp voltage – 45 kV and current intensity – 30 mA. The estimated concentrations (in %) of the analysed mineral components are given using the X-Pert computer program.

The content of the iron was analysed at Activation Laboratories Ltd. (Canada) by means of inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectroscopy (ICP-MS) methods using the Jarrell-Ash model Enviro and PerkinElmer STA/DSC 6000 model. To achieve this aim a 0.25 g sample was dissolved in 10 ml of HCl-HNO_3-$HClO_4$-HF at 200°C, subsequently the extracts were filled up to 10 ml with diluted aqua regiatrace. The parameters of the instrument used for inductively coupled plasma mass spectrometry (ICP-MS) were R_f power 900 W, argon plasma flow 16 l/min, argon nebulizer flow 0.8 l/min, and auxiliary argon flow 0.7 l/min.

The ^{57}Fe Mössbauer spectra were recorded at room temperature by a constant acceleration Mössbauer spectrometer equipped with a ^{57}Co(Rh) source (activity ~10 mCi). The absorber of metallic iron powder (α-Fe) was used for velocity and isomer shift calibrations of the Mössbauer spectrometer. The line width parameter G (full width at half maximum) of 0.35 mm/s for the outer line of α-Fe was obtained at room temperature. The numerical analysis of the Mössbauer spectra was performed with the use of the WMOSS program. The value of G for fitted subspectra was equal to 0.35 mm/s or 0.40 mm/s. Such values were close to the parameters presented in the literature for similar samples [13, 15]. The mineralogical analysis of the spectra was based on the Mössbauer mineral handbook [16].

Results and discussion

The minerals in samples 1l–5l are mainly quartz (30.0–36.7 wt%) and anhydrite (23.70–43.50 wt%) with a smaller quantity of muscovite (0.3–1.1 wt%). The minerals in samples 1d–5d are also mainly quartz (50.1–71.5 wt%) and anhydrite

Table 1. Minerals [wt%] in the fluidized fly and bottom ashes

Minerals	Fly ash		Bottom ash	
	Average	Range of variability	Average	Range of variability
Quartz	33.72	30.0–36.7	61.52	50.1–71.5
Anhydrite	31.04	23.7–43.5	18.58	12.8–26.3
Muscovite	0.78	0.3–1.1	1.26	0.7–1.7
Microcline	9.40	9.5–14.2	13.56	11.8–17.8
Calcite	7.42	6.4–9.9	2.66	1.5–5.4
Hematite	17.64	10.8–21.9	1.36	0.8–3.8
Aragonite	nd	nd	1.06	0.5–5.3

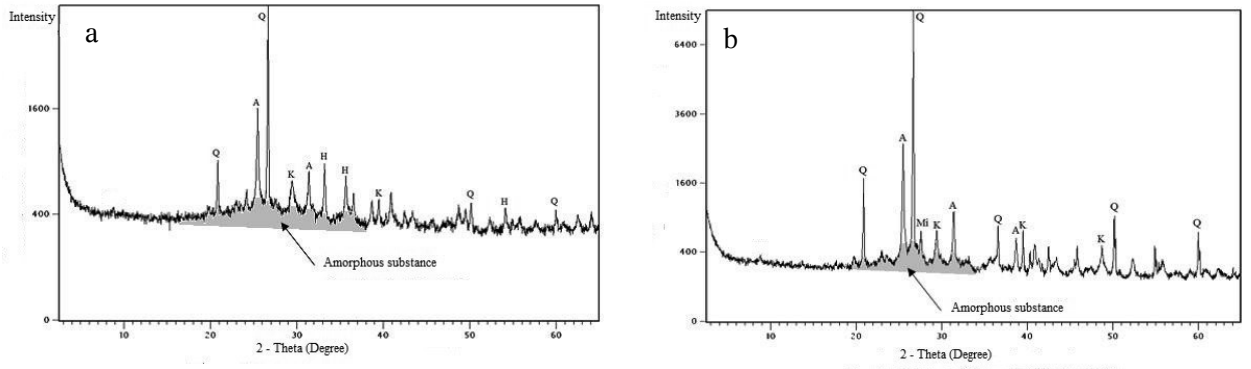

Fig. 1. XRD patterns of fly ash (1l) a) and bottom ash (1d) b) samples. Mineral abbreviations: K – calcite, Q – quartz, A – anhydrite, H – hematite and Mi – microcline. Amorphous substance is also selected.

(12.8–26.3 wt%) with smaller amounts of muscovite (0.7–1.7 wt%) and aragonite (0.5–5.3 wt%) (see Table 1). X-ray powder diffraction analyses show also that the amorphous phase constitutes about 60 wt% of the ashes. This estimate was obtained using the Rietveld method. Figure 1 shows XRD patterns for the investigated samples of fly and bottom ashes selected.

Samples of fly ash are rich in iron (5.03–5.88 vol.%; average 5.47 vol.%). The concentration of iron in the samples of bottom ash ranges between 2.69 and 4.07 vol.% (average 3.4 vol.%).

The Mössbauer spectra of fluidized bed samples from the ELCHO power plant in Chorzów are shown in Fig. 2. The hyperfine parameters derived from the fitting procedure are summarized in Tables 2 and 3. A small dispersion in the hyperfine parameters of the Mössbauer spectra can be related to the fact that ash particles originating from the coal combustion process in power plants take various morphological

Table 2. The Mössbauer hyperfine parameters of fly ash samples. IS – isomer shift, QS – quadrupole splitting, *H* – hyperfine magnetic field, *G* – full width at half maximum, *A* – area fraction of subspectra

Sample	IS [mm/s]	QS [mm/s]	*H* [T]	*G* [mm/s]	*A* [%]	Compound
1l	0.21	0.41	–	0.40	28.9	Fe^{3+}
	0.26	1.15	–		8.9	Muscovite
	1.19	1.92	–		2.0	
	1.22	3.15	–		3.7	
	0.37	–0.18	52.6	0.35	29.9	Hematite
	0.37	–0.20	51.5		33.6	
2l	0.24	0.31	–	0.40	23.6	Fe^{3+}
	0.25	0.91	–		14.0	Muscovite
	1.06	1.92	–		2.1	
	1.16	3.10	–		2.5	
	0.37	–0.18	52.4	0.35	37.0	Hematite
	0.37	–0.19	51.0		20.8	
3l	0.22	0.40	–	0.40	36.8	Fe^{3+}
	0.32	0.94	–		6.7	Muscovite
	1.19	1.92	–		2.3	
	1.12	3.10	–		1.7	
	0.39	–0.17	52.3	0.35	25.2	Hematite
	0.35	–0.19	51.5		27.3	
4l	0.24	0.36	–	0.40	21.3	Fe^{3+}
	0.32	1.15	–		12.4	Muscovite
	1.16	1.90	–		1.2	
	1.17	3.10	–		2.5	
	0.40	–0.24	52.6	0.35	27.1	Hematite
	0.33	–0.11	51.5		27.5	
	0.38	–0.24	49.5		8.1	
5l	0.20	0.35	–	0.40	16.5	Fe^{3+}
	0.18	0.55	–		14.5	
	0.48	0.66	–		5.1	Muscovite
	1.19	1.87	–		4.0	
	1.15	3.09	–		1.3	
	0.36	–0.17	52.4	0.35	32.1	Hematite
	0.39	–0.20	51.4		26.5	

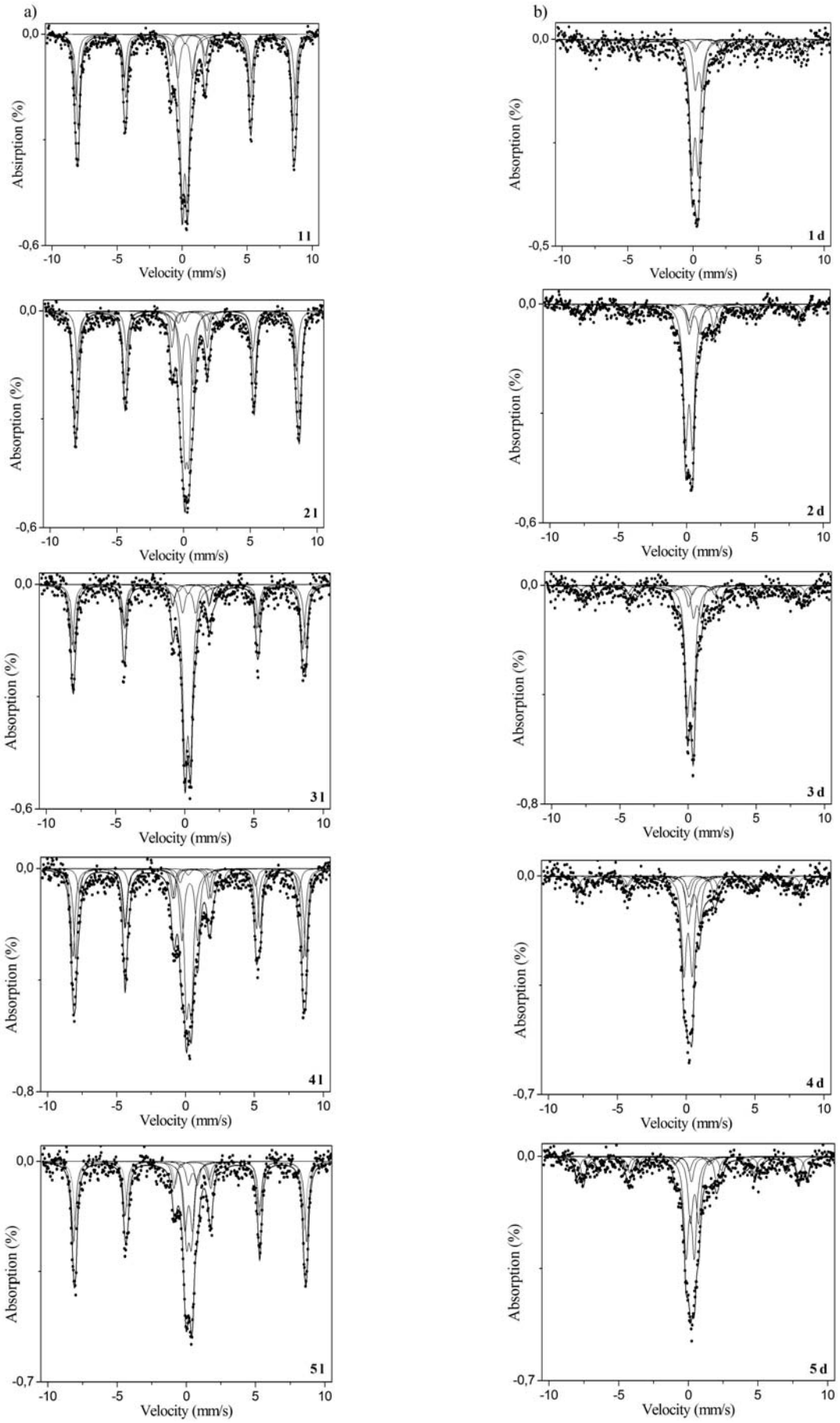

Fig. 2. Room-temperature Mössbauer spectra obtained for fly (a) and bottom (b) ashes from the ELCHO power plant in Chorzów. The fitted subspectra are presented on the investigated spectra.

forms of different sizes. On the whole, Fe^{3+} ions dominate in the fly ash samples. These ferric ions are located in the magnetic phase which is represented by hematite. Sextets connected with α-Fe_2O_3 contribute more than 50% to the Mössbauer spectra of each of the investigated samples of fly ash. The hematite content in fly ash samples is markedly higher due to oxidation during the combustion of the Fe-sulphates and carbonates as well as some dihydroxylation of goethite and lepidocrocite [17]. The second dominating component in the Mössbauer spectra of the fly ashes is the ferric doublet with an average isomer shift of about 0.22 mm/s and a contribution of more than 20%. It might be assumed that this doublet corresponds to amorphous Fe^{3+} in glass, which other authors have suggested [18–20] and XRD measurements also indicate a dominating contribution of the amorphous phase in the investigated ashes. It is important to realize that the amorphous and short-ordered phases are the least studied phases among the components of coal fly ashes since XRD, which is the method generally used to determine the mineralogy of samples, is useful for crystalline phases and less so for amorphous or short-ordered phases. The other non-magnetic components whose parameters are listed in Table 2 are connected with the small contribution of muscovite in all the investigated fly ashes.

From the Mössbauer spectral data (Table 3) it can be stated that the main iron-bearing source in the

Table 3. The Mössbauer hyperfine parameters of bottom ash samples

Sample	IS [mm/s]	QS [mm/s]	H [T]	G [mm/s]	A [%]	Compound
1d	0.15	0.48	–	0.40	46.9	Fe^{3+}
	0.44	0.53	–		18.1	Fe^{3+}
	1.25	2.15	–		4.8	Siderite
	1.15	1.81	–		3.9	
	0.42	–0.24	52.4		7.2	Hematite
	0.28	–0.02	49.8		10.5	Magnesioferrite
	0.31	–0.01	46.4		8.6	
2d	0.19	0.50	–	0.40	48.6	Fe^{3+}
	0.59	0.78	–		10.7	Fe^{3+}
	1.27	2.21	–		6.5	Siderite
	1.14	1.72	–		8.8	
	0.32	–0.24	52.2		6.6	Hematite
	0.35	–0.07	49.3		11.3	Magnesioferrite
	0.34	–0.01	44.1		7.5	
3d	0.17	0.45	–	0.40	43.5	Fe^{3+}
	0.67	0.56	–		11.6	Fe^{3+}
	1.19	2.30	–		8.3	Siderite
	1.14	1.65	–		3.7	
	0.40	–0.11	52.3		9.7	Hematite
	0.35	0.03	49.6		13.4	Magnesioferrite
	0.41	0.02	44.0		9.8	
4d	0.22	0.36	–	0.40	9.0	Fe^{3+}
	0.14	0.60	–		33.2	Fe^{3+}
	0.57	0.80	–		16.3	Fe^{3+}
	1.24	2.26	–		4.7	Siderite
	1.14	1.86	–		7.4	
	0.33	–0.14	51.0		12.0	Hematite
	0.27	–0.05	48.2		10.6	Magnesioferrite
	0.29	–0.01	43.5		6.8	
5d	0.14	0.59	–	0.40	29.8	Fe^{3+}
	0.45	0.60	–		19.5	Fe^{3+}
	1.24	2.28	–		4.5	Siderite
	1.14	1.82	–		8.1	
	0.32	–0.11	51.5		13.0	Hematite
	0.24	–0.07	48.1		15.8	Magnesioferrite
	0.29	–0.01	42.3		9.3	

bottom ashes, like in the fly ashes, is the paramagnetic ferric doublet that exhibits an isomer shift of between 0.14 mm/s and 0.22 mm/s. The abundance of this component is large in bottom ashes and ranges from 47% for sample 1d to 30% for sample 5d. Like for fly ashes, this doublet is related to amorphous Fe^{3+} in glass. In the Mössbauer spectral data another ferric doublet was identified with a contribution of about 11% for samples 2d and 3d to even as large as 20% for samples 1d and 5d. This component probably corresponds to the presence of $Fe^{3+}O(OH)$. Two ferrous doublets present in all bottom ash samples were identified as siderite (about 12% in abundance). Magnesioferrite was the dominating magnetic phase in bottom ash samples (about 20% in abundance). Apart from this magnetic component hematite was also identified. However, the XRD measurements could not detect some minerals visible on the Mössbauer spectra, which are connected with the small contents of iron in all the samples of bottom ash.

Conclusion

The techniques applied proved to be useful in the investigation to better describe the modes of occurrence of iron-bearing species in the by-products of coal combustion. Also, the qualitative consistency of the results of Mössbauer spectrometry and chemical analysis allow the construction of a future project concerning the comprehensive investigation of the iron speciation in fluidized beds with the aim of achieving a better understanding of the mineral transformations that occur during the combustion of coal.

XRD analysis suggested that the fly and bottom fluidized ashes consist mainly of quartz and calcium-based minerals in the form of anhydrite and calcite. The total iron concentration in wastes is between 3.4 vol.% for bottom ash and 5.47 vol.% for fly ash.

In general, after comparing the hyperfine parameters obtained from the Mössbauer spectroscopy of fluidized beds in addition to fly and bottom ash samples originating from the ELCHO power plant in Chorzów, as well as the observations of XRD, it may be concluded that the fly and bottom ash samples were of similar elemental composition, but exhibited different degrees of contribution. In the investigated samples Fe^{3+} ions dominate. The major iron-bearing components identified in fly ash were hematite and paramagnetic ferric iron in the amorphous phase of the samples. Fly ash produced as a result of the combustion of coal was also the main source of anthropogenic particles which can lead to an increase in its magnetic susceptibility in the environment. Paramagnetic ferric iron in the amorphous phase dominated in the bottom ash samples but some minerals, e.g. magnesioferrite, hematite, muscovite and siderite, were also present.

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